

Sulfur Removal from Reformate

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Objectives

Develop a sulfur removal process for on-board fuel processing to meet DOE targets for hydrogen sulfide (H_2S) removal to <10 ppbv H_2S in reformat by 2010, a reactor volume of <0.06 L/kW_e and weight of <0.06 kg/kW_e, and operation at a gas-hourly space velocity (GHSV) of 50,000 h⁻¹.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup

Approach

- Identified Cu oxides as candidate materials based on the H_2S equilibrium partial pressure for candidate adsorbents (metal sulfide- H_2S equilibrium).
- Synthesize mixed metal oxides consisting of CuO/Cu₂O and another transition metal oxide to stabilize copper in its oxide forms.
- Conduct experimental studies in a microreactor system to evaluate the H_2S concentration in the effluent as a function of temperature, flow rate, water content, and the gas composition for candidate mixed metal oxides.

Accomplishments

- Synthesized various mixed metal oxides consisting of CuO/Cu₂O and screened them for H_2S uptake in a microreactor system.
- Determined the effects of operating temperature, flow rate, water content, and gas composition on the performance of H_2S removal by a copper oxides-based composition.
- Demonstrated that a copper oxides-based composition reduced H_2S concentration from 10 ppmv to <50 ppbv from a simulated reformat.

Future Directions

- Evaluate H_2S uptake for the materials supported on the structured form.
- Characterize materials to improve performance and address stability issues.
- Optimize the composition and materials processing and work with industrial collaborator.

Introduction

On-board reforming of gasoline is one option being considered for supplying H_2 for polymer electrolyte fuel cell (PEFC) powered propulsion systems for automobiles and light-duty vehicles. Under reforming conditions, the sulfur present in gasoline is converted to H_2S . Although new Environmental Protection Agency (EPA) regulations will reduce the sulfur content of gasoline to <80 ppmw beginning in 2006, reformat produced from these gasolines will still contain ~10 ppmv H_2S . Concentrations of H_2S as low as 50 ppbv have been shown to irreversibly poison the PEFC catalysts.¹ As a consequence, DOE has established a target of <10 ppbv H_2S in reformat by 2010.

Two different approaches, liquid-phase desulfurization of the fuel prior to reforming² and gas-phase desulfurization of reformat after reforming, are being considered for on-board sulfur removal. There is a concern with liquid-phase desulfurization that H_2S will still need to be removed from reformat. Gas-phase desulfurization requires that the reforming catalyst be sulfur-tolerant. Our focus is on developing adsorbents for gas-phase desulfurization.

Zinc oxide (ZnO) is used for sulfur removal in the production of H_2 from natural gas for ammonia and methanol synthesis. For on-board fuel processing using ZnO, thermodynamic equilibrium predicts that a temperature of <250°C is required to reduce the H_2S concentration to <10 ppbv. We have observed that the concentration of H_2S in reformat increased as the temperature decreased below 300°C due to unfavorable kinetics, making ZnO unsuitable for on-board fuel processing.³ Copper oxides (CuO and Cu_2O) have among the highest sulfidation equilibrium constants for metal oxides and can potentially achieve parts-per-billion concentrations of H_2S in reformat. However, under fuel processing conditions, Cu_2O/CuO are reduced to metallic Cu. The sulfidation equilibrium for metallic Cu is significantly less than that of Cu oxides, resulting in reduced desulfurization efficiency. Research has focused on combining CuO/Cu_2O with other metal oxides to stabilize the oxide form,⁴ which is the approach that we are investigating.

Approach

Compositions consisting of Cu and a second transition metal oxide dispersed on a high surface area support, such as $\gamma-Al_2O_3$, were prepared by either co-impregnation or successive impregnation methods using nitrate salts as precursors. The H_2S desulfurization performance of these compositions was evaluated in a microreactor system. In a typical test, a sample of up to 2 mL was exposed to a synthetic reformat (10-40 ppmv H_2S , 29% H_2 , 20% H_2O , 6% CO, 6.1% CO_2 , 0.2% CH_4 , balance N_2) at temperatures ranging between 200-400°C and at GHSVs ranging between 2000-50,000 h^{-1} . The H_2S concentration in the effluent from the reactor was measured using a gas chromatograph (GC) equipped with a flame photometric detector (FPD) with a detection limit of 200 ppbv H_2S and an on-line lead-acetate based H_2S analyzer with a detection limit of 20 ppbv H_2S .

Results

Figure 1 shows a typical H_2S breakthrough curve (i.e., H_2S concentration in the effluent as a function of time) for these sorbents at 350°C and a GHSV of 2000 h^{-1} with a feed H_2S concentration of 40 ppmv. All compositions tested, including Cu alone, exhibited two stages of H_2S breakthrough. During the first stage, they reduced the H_2S concentration below detection limit of the FPD. During the second stage, they reduced the H_2S concentration to ~10 ppmv. The second stage is believed to be associated

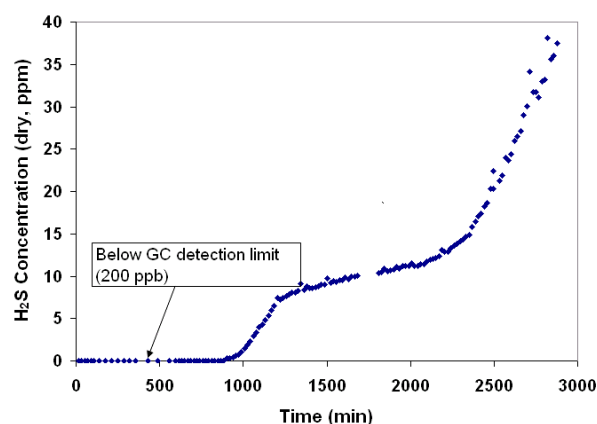


Figure 1. The H_2S Breakthrough Curve for Cu+B at 350°C and a GHSV of 2000 h^{-1}

with the sulfidation of metallic copper since the observed H_2S concentration of 10 ppmv is close to that predicted by thermodynamic equilibrium (7.2–10.6 ppmv at 350–380°C) for metallic Cu; however, this has not been experimentally confirmed. These materials did show different sulfur uptake capacities as shown in Table 1. The highest sulfur uptake capacities were shown by compositions identified as Cu+B and Cu+C.

The Cu+C system was chosen for further study to determine the effect of various operating parameters including temperature, GHSV, and the water content in reformat on H_2S removal. Temperature significantly affected H_2S removal performance, as shown in Figure 2. The H_2S concentration was reduced from 10 ppmv to <50 ppbv at 200 and 300°C; however, a longer breakthrough time was observed at 200°C, indicating a higher H_2S uptake capacity. At 200°C, the reduction of copper oxides to metallic Cu is less favorable, suggesting more of the Cu may be in the oxide form, which would favor desulfurization.

The effect of GHSV at 200°C is shown in Figure 3. Although breakthrough time decreased significantly as the GHSV was increased from 10,000 to 50,000 h^{-1} , similar sulfidation efficiencies (~20 ppbv) and Cu utilizations (~60%) were observed at both GHSVs. When the temperature was increased to 350°C, the performance decreased significantly at the higher GHSV. The sulfidation efficiency was 25 ppbv and the Cu utilization was 15% at a GHSV of 10,000

h^{-1} , which decreased to 200 ppbv and 5%, respectively, at a GHSV of 50,000 h^{-1} . This implies that lower operating temperatures are desirable if the GHSV target is to be met.

The effect of the H_2O concentration in the reformat on H_2S removal performance is shown in Figure 4. The pre-breakthrough H_2S concentration increased as the H_2O concentration increased from 11 to 30 vol%, consistent with the reaction equilibrium (e.g., $\text{Cu}_2\text{O} + \text{H}_2\text{S}(\text{g}) = \text{Cu}_2\text{S} + \text{H}_2\text{O}(\text{g})$). Since H_2O is a product of the sulfidation reaction, increasing the H_2O concentration in the reformat shifts equilibrium towards the reactants, leading to a higher H_2S concentration.

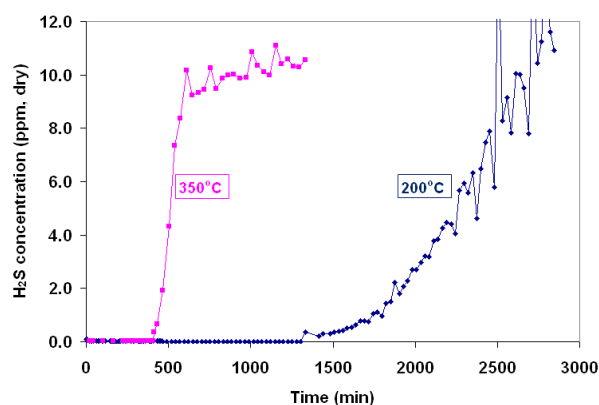


Figure 2. The Effect of Temperature on H_2S Breakthrough for Cu+C at a GHSV of 10,000 h^{-1}

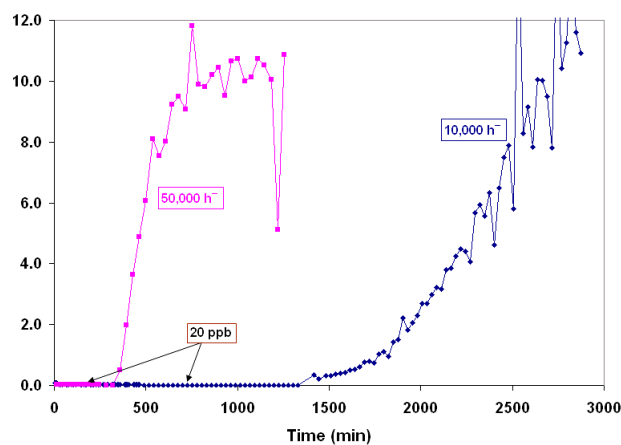


Figure 3. The Effect of GHSV on H_2S Breakthrough for Cu+C at 200°C

Table 1. Copper Utilization for Sulfidation of Binary Oxides of Copper and a Second Transition Metal

Sorbent formulation	Surface area (m^2/g)	Sulfur uptake (% based on Cu content) ^a
Cu+A/ Al_2O_3	197.9	37.3
Cu+B/ Al_2O_3	199.5	57.9
Cu+C/ Al_2O_3	211.3	53.9
Cu+D/ Al_2O_3	201.5	44.0
Cu+E/ Al_2O_3	202.3	32.8
Cu/ Al_2O_3	258.8	36.3

^aCalculated based on H_2S uptake until breakthrough occurs (1 ppmv H_2S).

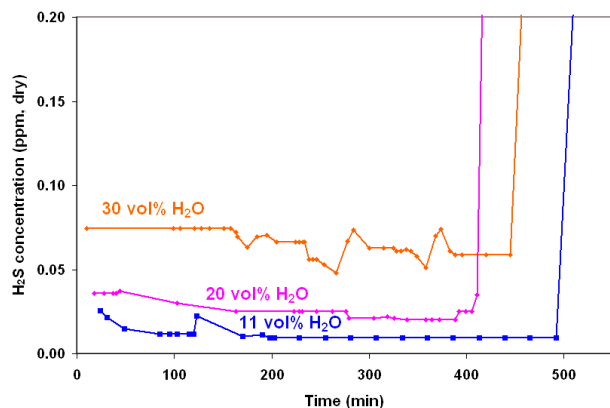


Figure 4. The Effect of H₂O Concentration in the Reformat on H₂S Breakthrough for Cu+C at 350°C and a GHSV of 10,000 h⁻¹

Conclusions

- Binary oxides containing Cu are capable of reducing the H₂S concentration from 10 ppmv to <50 ppbv in reformates containing 30% H₂ and 20% H₂O at temperatures ranging from 200-350°C and GHSVs ranging from 10,000-50,000 h⁻¹.
- Lower operating temperatures, lower H₂O concentrations, and lower GHSVs are desirable to meet DOE targets.

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FY 2003 Publications/Presentations

1. X. Wang, T. Krause, and R. Kumar, "Sulfur Removal from Reformat," extended abstract, pre-prints, Petroleum Chemistry Division, the 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003.